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Final Report

RESEARCH ON THE KINETICS OF PHASE CHANGES IN SOLIDS

John P. Hirth  
Department of Metallurgical Engineering

For the Period  
December 15, 1984 - February 28, 1985

DEPARTMENT OF THE NAVY  
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Arlington, Virginia 22217

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FIELD	GROUP	SUB. GR.													
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Research on the kinetics of phase transformations is summarized. Topics include nucleation and growth of crystals from the vapor phase, thin film interface structure, diffusional growth of interfacial layers, and displacement reactions at interfaces.															
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FINAL TECHNICAL REPORT ON RESEARCH PERFORMED  
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ONR Scientific Officer: Dr. Philip A. Clarkin  
Principal Investigator: Dr. J. P. Hirth

"RESEARCH ON THE KINETICS OF PHASE CHANGES IN SOLIDS"

I. Introduction

The research on this project involved four major areas with the emphasis changing over the fifteen years of funding. Initially, the work emphasized nucleation and growth of crystals from the vapor phase. The second area was that of interface structure between thin films and substrates. Later work focussed on interface reactions in solids including growth of multiphases by interdiffusion, formation of multiple scales in oxidation, and displacement reactions. Finally, work was begun on the breakdown of diffusional blocking layers by interdiffusion processes.

In order in the following material, sections are presented on: the highlights of the research; technical reports, publications and recognitions; and participation in the work.

II. Research Highlights

A. Vapor Deposition

Quantitative explanations for single crystal sublimation rates in terms of surface ledge motion were made and verified by surface morphology measurements. A theory was developed for the influence of surface charge on crystal growth, sublimation and surface morphology and was verified in work on zinc oxide. Follow up work on this topic has continued with collaborative work with the groups of Z. A. Munir at the University of California-Davis and M. J. Yacaman at the University of Mexico as indicated on the publication list. This work

has direct applications in the burgeoning field of thin film deposition in electronic devices, including multiple-beam epitaxy and chemical vapor deposition.

#### B. Thin Film Interfaces

The first complete calculation of the elastic field of a set of interface dislocations in a thin film-thick substrate couple was performed. The critical thickness for loss of coherency was predicted and verified in thin film interdiffusion experiments. This work has implications for the work of current interest on the stability of strained superlattices.

#### C. Reactions at Interfaces

A theory for the rate of formation of layers in multiple phase layer growth was developed for the cases of metallic interdiffusion couples and oxidation. Work on interdiffusion in the Ag-Zn system verified the theory as did a survey of oxidation data for Cu and Fe. A theory had been developed by Rapp et al. to explain the breakdown of layer growth in a displacement reaction of the type  $A_2O + B \longrightarrow BO + A_2$  where A and B are metals. New theories were developed to explain the types of aggregate structures resulting from the breakdown and were verified in simple oxide and sulfide displacement reactions and in more complex mixed oxide-carbide displacement reactions. This work has practical applications in producing a fine structure of metal or compound (oxide) penetrated by  $\mu\text{m}$  scale void tunnels. It also has implications, as yet little exploited, for the creation of new microstructures in the processing of alloys by the rapid-solidification-hot isostatic compaction route.

Most recently, a finite difference model has been developed to predict the rate of breakdown of a blocking layer by interdiffusion.

### III. Publications and Recognitions

#### A. Technical Reports

1. Technical Report No. 1, "Surface Morphology of Sublimated Crystals of Cadmium and Zinc Sulfides," by Z. A. Munir and, J. P. Hirth, September 1970.
2. Technical Report No. 2, "Nucleation of a Disc-shaped Hole in a Low Index Surface and at a Dislocation," by W. H. Robinson and J. P. Hirth, December, 1970.
3. Technical Report No. 3, "Epitaxial Deposition of Silver on Molybdenite," by G. Pilkington and J. P. Hirth, August, 1971.
4. Technical Report No. 4, "Morphology of Thermally Etched Basal Surfaces of Cadmium Selenide," by Z. A. Munir, L. Seacrist and J. P. Hirth, March, 1972.
5. Technical Report No. 5, "Influence of Surface Charge and Surface Structure on the Sublimation of Ionic Crystals," by D. W. Short, R. A. Rapp and J. P. Hirth, October, 1972.
6. Technical Report No. 6, "Some Comments on Heterogeneous Nucleation from the Vapor Phase," by J. P. Hirth, March, 1973.
7. Technical Report No. 7, "Forces Acting on Misfit Dislocations During Interdiffusion," by K. Shinohara and J. P. Hirth, October, 1973.
8. Technical Report No. 8, "The Behavior of Misfit Dislocations During Interdiffusion," by K. Shinohara and J. P. Hirth, October, 1973.
9. Technical Report No. 9, "The Sublimation of Basal Surfaces of Zinc Oxide," by J. E. McVicker, R. A. Rapp and J. P. Hirth, December, 1974.
10. Technical Report No. 10, "Critical Thickness for loss of Coherency in Epitaxial Bimetals," by K. Shinohara and J. P. Hirth, November, 1975 (included reprints of publication based on Tech. Report No. 9).
11. Technical Report No. 11, "Elastic Fields of Line Defects in a Cracked Body," by J. P. Hirth and R. H. Wagoner, January, 1976.
12. Technical Report No. 12, "Hydrogen Problems in Energy-Related Technology," J. P. Hirth and H. H. Johnson, March, 1976.
13. Technical Report No. 13, "Mechanical Failures-Implications for Science," J. P. Hirth, June, 1976.
14. Technical Report No. 14, "A Theory of Multiphase Binary Diffusion," S. R. Shatynski, J. P. Hirth and R. A. Rapp, December, 1976.
15. Technical Report No. 15, Effects of Surface Imperfections on the Nucleation of Gold on NaAl," M. J. Yacaman and J. P. Hirth, March, 1977.

16. Technical Report No. 16, "Vaporization Kinetics of NaCl," R. H. Wagoner and J. P. Hirth, January, 1978.
17. Technical Report No. 17, "Kinetics of the Displacement Reaction Between Fe and Cu<sub>2</sub>O at Temperatures Between 800 and 1050°C," G. J. Yurek, R. A. Rapp and J. P. Hirth, May, 1979.
18. Technical Report No. 18, "Displacement Reactions Between Selected Metals and Sulfides," S. R. Shatynski, J. P. Hirth and R. A. Rapp, July, 1979.
19. Technical Report No. 19, "Cleavage Ledges and Interface Dislocations on Suzuki Phases in NaCl," M. J. Yacaman, A. Gomez R. and J. P. Hirth, September, 1979.
20. Technical Report No. 20, "Adsorption at Grain Boundaries and Its Effect on Decohesion," J. P. Hirth, April, 1980.
21. Technical Report No. 21, "Multilayer Diffusional Growth in Silver-Zinc Alloys," D. S. Williams, R. A. Rapp and J. P. Hirth, June, 1981.
22. Technical Report No. 22, "Hydrogen Induced Delayed Failure of High Strength Steel Wires," D. C. Langstaff, G. Meyrick and J. P. Hirth, November, 1981.
23. Technical Report No. 23, "Mechanism of the Solid State Displacement Reaction Iron and Nickel Oxide at 1000°C," C. Tangchitvittaya, J. P. Hirth and R. A. Rapp, April, 1982.
24. Technical Report No. 24, "Oxidation of Fe-Mn-Al Alloys at 850°C," and 1000°C," by J. P. Sauer, R. A. Rapp and J. P. Hirth, August, 1983.
25. Technical Report No. 25, "Effect of UV Illumination on the Sublimation of Basal Surfaces of Zinc Oxide," by D. A. Carey, R. A. Rapp and J. P. Hirth, October 1983.
26. Technical Report No. 26, "Oxidation of Ternary Co-Cr-W Alloys," by S. Espevik, P. L. Daniel, R. A. Rapp and J. P. Hirth, August, 1984.
27. Technical Report No. 27, "Hydrogen Attack in Austenitic Stainless Steel," by M. J. Yacaman, T. A. Parthasarathy and J. P. Hirth, October, 1984.

#### B. Publications

1. J. P. Hirth, G. M. Pound and G. R. St. Pierre, "Bubble Nucleation," Metallurgical Transactions, 1, 939 (1970).
2. Z. A. Munir and J. P. Hirth, "The Surface Morphology of Sublimated Crystals of Cadmium and Zinc Sulfides," Journal of Applied Physics, 41, 2697 (1970).
3. W. H. Robinson and J. P. Hirth, "The Nucleation of a Disc-shaped Hole at a Dislocation-surface Intersection," Journal of Crystal Growth, 7, 262 (1970).



4. T. Surek, G. M. Pound and J. P. Hirth, "Ledge Dynamics in Crystal Evaporation," *Journal of Chemical Physics*, 55, 5157 (1971).
5. J. P. Hirth, "Discussion of Bubble Nucleation," *Transactions ASME-Journal of Basic Engineering*, 92, 702 (1970).
6. Z. A. Munir, L. S. Seacrist and J. P. Hirth, "Morphology of Thermally Etched Basal Surfaces of Cadmium Selenide," *Surface Science* 28, 37 (1971).
7. G. Pilkington and J. P. Hirth, "Epitaxial Deposition of Silver on Molybdenite," *Surface Science* 29, 363 (1972).
8. J. P. Hirth, "A Dislocation Mechanism for Phase Transformation," in "Fundamental Aspects of Dislocation Theory," NBS Special Pub., 317, 1970, p. 547.
9. D. W. Short, R. A. Rapp and J. P. Hirth, "Influence of Surface Charge and Surface Structure on the Sublimation of Ionic Crystals," *Journal of Chemical Physics*, 57, 1381 (1972).
10. J. P. Hirth, "Influence of Grain Boundaries on Mechanical Properties," *Metallurgical Transactions*, 3, 3047 (1972).
11. J. P. Hirth, "Some Comments on Heterogeneous Nucleation Theory," *Journal of Crystal Growth*, 17, 63 (1972).
12. T. Surek, J. P. Hirth and G. M. Pound, "The Back-force Effect at Repeated Nucleation Sources in Crystal Evaporation and Dissolution Processes," *Journal of Crystal Growth* 18, 20 (1973).
13. K. Shinohara and J. P. Hirth, "Forces Acting on Misfit Dislocations During Interdiffusion," *Philosophical Magazine* 27, 883 (1973).
14. K. Shinohara and J. P. Hirth, "The Behavior of Misfit Dislocations During Interdiffusion," *Thin Solid Films* 16, 345 (1973).
15. T. Surek, G. M. Pound and J. P. Hirth, "Spiral Dislocations Dynamics in Crystal Evaporation," *Surface Science* 41, 77 (1974).
16. G. J. Yurek, J. P. Hirth and R. A. Rapp, "The Formation of Two Phase, Layered Scales on Pure Metals," *Oxide. of Met.* 8, 265 (1974).
17. K. Shinohara and J. P. Hirth, "Critical Thickness for Loss of Coherency in Epitaxial Bimetals," *Jap. J. Appl. Phys., Suppl.* 2, 629 (1974).
18. J. E. McVicker, R. A. Rapp and J. P. Hirth, "Sublimation of Basal Surfaces of Zinc Oxide," *J. Chem. Phys.*, 63, 2646 (1975).
19. J. P. Hirth and H. H. Johnson, "Hydrogen Problems in Energy Related Technology," *Corrosion* 32, 3 (1976).
20. J. P. Hirth and R. H. Wagoner, "Elastic Fields of Line Defects in a Cracked Body," *Int. J. Solids Struc.* 12, 117 (1976).

21. J. P. Hirth, "Mechanical Failures: Implications for Science, in N.B.S. Spec. Pub. 423, "Mech. Failures," U.S. Gov't. Print Off. (1976) 181.
22. S. R. Shatynski, J. P. Hirth and R. A. Rapp, "A Theory of Multiphase Binary Diffusion," *Acta Metallurgica*, 24, 1071 (1976).
23. M. J. Yacaman and J. P. Hirth, "Effects of Surface Imperfections on the Nucleation of Gold on Sodium Chloride," *Thin Solid Films*, 38, 215 (1976).
24. M. J. Yacaman, T. Ocana Z., A. M. Sonnemann and J. P. Hirth, "The Back-Force Effect and its Influence on Sublimation of Alkali Halide Single Crystal Surfaces," *Journal of Crystal Growth*, 37, 37 (1977).
25. J. P. Hirth and R. A. Rapp, "The Diffusional Growth of a Scale with Variable Composition, Diffusivity and Molar Volume," *Oxidation of Metals*, 11, 57 (1977).
26. Z. A. Munir and J. P. Hirth, "Transient Phenomena in the Sublimation of Cadmium Sulfide," *Journal of Electronic Materials*, 6, 409 (1977).
27. R. A. Wagoner and J. P. Hirth, "Vaporization Kinetics of Sodium Chloride," *Journal of Chemical Physics*, 67, 3074 (1977).
28. Z. A. Munir and J. P. Hirth, "Transient Effects in Sublimation of CdS," *Journal of Electronic Materials*, 6, 409 (1977).
29. S. R. Shatynski, J. P. Hirth and R. A. Rapp, "Solid State Displacement Reactions Between Selected Metals and Sulfides," *Metallurgical Transactions*, 10A, 591 (1979).
30. M. J. Yacaman, A. Gomez and J. P. Hirth, "Cleavage Ledges and Interface Dislocations on Suzuki Phases in NaCl," *Philosophical Magazine*, 39A, 709 (1979).
31. J. P. Hirth, "Adsorption at Grain Boundaries and Its Effect on Decohesion," *Phil. Trans. Roy. Soc. (London)*, 139 (1980).
32. S. Espevik, R. A. Rapp, P. L. Daniel and J. P. Hirth, "Oxidation of Ni-Cr-W Ternary Alloys," *Oxidation of Metals*, 14, 85 (1980).
33. J. P. Hirth and D. A. Rigney, "Microstructural Models for Friction and Wear," in "Strength of Metals and Alloys," eds. P. Haasen et al., Pergamon, Oxford, 1980, 3, p. 1483.
34. M. J. Yacaman, Z. A. Munir and J. P. Hirth, "The Influence of an Electric Field on the Sublimation Kinetics of Alkali Halide Surfaces," *Journal of Crystal Growth*, 49, 475 (1980).
35. J. P. Hirth, "Effect of Hydrogen on the Properties of Iron and Steel," *Metallurgical Transactions*, 11A, 861 (1980).

36. D. S. Williams, R. A. Rapp and J. P. Hirth, "Multilayer Interdiffusion in the Ag-Zn System," Metallurgical Transactions, 12A, 639 (1981).
37. Z. A. Munir and J. P. Hirth, "The Nature and Role of Surface Charge in Ceramics," in "Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems," eds. J. Pask and A. G. Evans, Plenum, New York, 1981, p. 23.
38. D. Langstaff, G. Meyrick and J. P. Hirth, "Delayed Failure of Hydrogen Charged Steel Wires," Corrosion, 37, 429 (1981).
39. C. Tangchit, J. P. Hirth and R. A. Rapp, "Solid-State Displacement Reaction Between Iron and Nickel Oxide at 1000°C, Metallurgical Transactions, 13A, 585 (1982).
40. J. P. Sauer, R. A. Rapp and J. P. Hirth, "Oxidation of Iron-Manganese-Aluminum Alloys at 850°C and 1000°C," Oxidation of Metals, 18, 285 (1982).
41. S. J. Czyzak, J. P. Hirth and R. G. Tabak, "The Formation and Properties of Grains in the Interstellar Medium," Vistas in Astronomy, 25, 337 (1982).
42. S. Espevik, P. Daniel, R. A. Rapp and J. P. Hirth, "Oxidation of Co-Cr-W Alloys," Oxidation of Metals, 20, 37 (1983).
43. J. P. Hirth and D. A. Rigney, "The Application of Dislocation Concepts to Friction and Wear," in vol. 6 of "Dislocations in Solids," F. R. N. Nabarro, ed. (North-Holland, Amsterdam, 1983), p. 1.
44. Z. A. Munir, E. K. Chieh and J. P. Hirth, "Effects of Electrostatic Fields on the Ledge Structures Produced by Evaporation of Alkali-Halide Crystals," Journal of Crystal Growth, 63, 244 (1983).
45. D. Carey, J. P. Hirth and R. A. Rapp, "Influence of Ultraviolet Irradiation on the Sublimation of Zinc Oxide," Journal of Chemical Physics, 79, 3160 (1983).
46. M. J. Yacaman, T. A. Parthasarathy and J. P. Hirth, "Hydrogen Attack in an Austenitic Stainless Steel," Metallurgical Transactions, 15A, 1485 (1984).

#### C. Recognitions

1. A micrograph from publication B-2 was used as the cover photograph for J. Appl. Phys.
2. Publication B-11 was the Campbell Lecture of J. P. Hirth in 1972.
3. Publications B-17 and B-26 were incorporated in the Campbell Lecture of R. A. Rapp in 1982.
4. Publication B-3C was the IMD Lecture of J. P. Hirth in 1980.

#### IV. Participants

##### A. Professors

1. J. P. Hirth, O.S.U.
2. R. A. Rapp, O.S.U.
3. G. Meyrick, O.S.U.

##### B. Collaborations of J. P. Hirth with other groups.

1. D. A. Rigney, O.S.U.
2. G. W. Powell, O.S.U.
3. Z. A. Munir, University of California, Davis
4. Y. J. Yacaman, University of Mexico.

##### C. Postdoctorate Research Fellows

1. G. Pilkington, now at Intel.
2. S. Espevik, Norway (now deceased).

##### D. Graduate Students Receiving Ph.D. Degrees

1. T. Surek, now at SERI.
2. D. W. Short, now at Lawrence Livermore.
3. K. Shinohara, now a Professor at Ehima University, Japan.
4. G. J. Yurek, now a Professor at M.I.T.
5. J. E. McVicker, now with Caterpillar Tractor.
6. R. H. Wagoner, now a Professor at O.S.U.
7. S. R. Shatynski, was a Professor at R.P.I. (now deceased).
8. D. S. Williams, now at Bell Labs (Murray Hill).
9. D. Langstaff, now at Hanford (Battelle).
10. C. Tangchitvittaya, now with Exxon in Thailand.
11. D. Carey, now with the U.S. Air Force.
12. R. Shook, now at Bell Labs (Allentown).

##### E. Graduate Students Receiving M.S. Degrees

1. A. Sonnemann, now in Mexico.
2. P. Daniel, now with Teledyne.
3. J. Sauer, now with Alcoa.

**END**

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